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VARIATION OF REACTION RATE WITH VIBRATIONAL STATE

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Chemical reactions in general are studied with systems whose components have a thermal distribution. The interpretation of such experiments requires averaging elementary reactions over many initial quantum states. Very little can be inferred about the relative reactivity of molecules in the individual quantum states beyond the rough indication provided by the variation of the reaction rate with temperature. A much more direct and fundamental type of information comes from experiments in which at least one of the participating species is sorted into known states of quantization before reaction.

A method presently available for the selection of states is high-resolution molecular-beam spectroscopy. This note is concerned with the reaction commonly used for the detection of alkali halide beams—dissociation and ionization on a hot tungsten surface. Evidence will be presented which indicates that the rate of dissociation depends on the vibrational state of the incident molecules.

The Beam Experiment.—Marple and Trishka¹ have recently studied the radio-frequency spectrum of lithium chloride by the molecular-beam electric-resonance method. In their apparatus (see Fig. 1), molecules in the state of angular momentum $J = 1$ and space quantization $M_J = 1$ are selected by an inhomogeneous de-

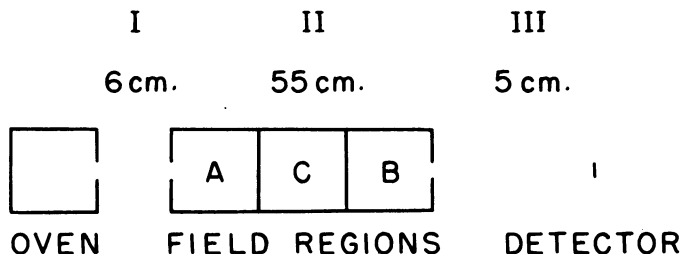


FIG. 1.—Schematic diagram of the apparatus of Marple and Trishka.

flecting field A . In the region of the homogeneous electric field C , transitions to the state $J = 1, M_J = 0$ are induced by monochromatic radio-frequency radiation. A second inhomogeneous field B then deflects only the molecules with $J = 1, M_J = 0$ to the tungsten-wire detector. The frequency for the electric hyperfine transition is slightly dependent upon the vibrational state of the molecule, and the high resolution permits separate resonances to be observed for four different vibrational states, $v = 0, 1, 2, 3$. Thus, except for background from scattered molecules and for molecules which change their state by radiation processes between leaving the last inhomogeneous field B and reaching the detector, the molecules reaching the tungsten wire for a given resonant frequency of the r.f. field are in a completely specified state with respect to electronic energy (ground state), vibrational energy (v , as selected by the r.f.), angular momentum ($J = 1$), and space orientation of the angular momentum ($M_J = 0$).

Reaction of LiCl on a Tungsten Wire.—The over-all reaction taking place at the hot tungsten wire is



The current of lithium ions is detected with a mass spectrometer and ion multiplier. In this "flip-in" type of beam experiment only about 10^5 molecules per second reach the detector,² so that the number of those which interact with each other is negligible. The tungsten wire is estimated² to be at $1,400 \pm 200^\circ \text{K}$. (At this temperature the surface is actually covered with a monolayer of molecular oxygen.³)

Table 1 gives the relative populations of vibrational states calculated from the oven temperature and the known vibrational frequency,⁴ under the assumption that the molecules leaving the oven are harmonic oscillators in thermal equilibrium. Spontaneous vibrational transitions during transit slightly alter the relative numbers reaching the detector, as shown.

The relative ion currents observed by Marple and Trischka for the hyperfine resonances corresponding to molecules in different vibrational states are listed in the fourth column of Table 1. It is seen that the relative intensities I_v are not pro-

TABLE 1
COMPARISON OF VIBRATIONAL STATES

VIB. QUANT. NUMBER v	REL. POP. LEAVING OVEN* N_v'	REL. POP. REACHING WIRE N_v	OBS. REL. ION CURRENT I_v	I_v/N_v	
				Obs.	Calc.†
0	1	1	1	1	1
1	0.28 ± 0.04	0.27	0.38	1.4	1.4
2	0.078 ± 0.02	0.075	0.15	2.0	2.1 ± 0.07
3	0.022 ± 0.01	0.020	0.058	2.9	3.3 ± 0.2

Effective
vib.
temp.‡

805

772

$1,074^\circ \text{K}$.

* For $805 \pm 100^\circ \text{K}$; the uncertainties apply also to N_v .

† Only the uncertainty due to that in the temperature of the wire ($1,400 \pm 200^\circ \text{K}$) is indicated. It should be noted that if a different value for the oven temperature were used to calculate N_v , the experimental values of I_v/N_v would differ considerably from those listed. However, the corresponding adjustment of k_e/k to fit I_1/N_1 of course changes the theoretical values, and similar agreement is found for any oven temperature in the range 700° – 900°K .

‡ The temperature found by fitting a Boltzmann factor for the vibrational frequency $\nu = 715 \text{ cm}^{-1}$.

portional to the calculated number of molecules reaching the detector. The data is well fitted by

$$\frac{I_v}{N_v} = (1.4)^v = \exp(0.34v). \quad (2)$$

If (merely for characterization) a Boltzmann factor is fitted to the relative ion currents $I_v = \exp(-h\nu/kT)$, then $T = 1,074^\circ \text{ K}$. This deviation seems well outside both the experimental errors and the uncertainty in measurement of the oven temperature,¹ $805 \pm 100^\circ \text{ K}$., and the vibrational frequency,⁴ $715 \pm 15 \text{ cm}^{-1}$. Corrections for the background from scattered molecules and losses from the beam and ion currents do not discriminate between the vibrational states. Saturation of the r.f. resonances could cause errors which differ with ν , and care was taken to avoid this.⁵ Although the calculation of N_v was based upon the assumption that the molecules leaving the oven are harmonic oscillators in thermal equilibrium with respect to vibration, there would have to be a very large deviation to cause a discrepancy comparable with the ratio found in equation (2). Translational equilibration is of minor importance, since this enters only in computing the small radiative correction.

The strong increase of I_v/N_v with ν therefore will be interpreted to mean that the detecting reaction depends upon the vibrational state of the incident lithium chloride molecules. Equation (2) is then the relative rate constant for the over-all reaction (1) as a function of the initial vibrational state.

Several kinds of evidence⁶ indicate that reaction (1) occurs by dissociation of the alkali halide molecule into atoms, followed by ionization of the alkali atom. The dependence of the net reaction on the vibrational state of the incident molecules is then to be sought in the probability of capture by the surface, the residence period on the surface, and the dissociation process.

Molecular properties such as the dipole moment and polarizability which evidently are responsible for the attraction to the surface vary slowly with vibrational state. It is therefore unlikely that the capture probability could change significantly with vibrational state.

If almost every molecule striking the surface were to stick until it dissociated, any dependence of the reaction on initial state would be ineffective. Thus, in order for I_v/N_v to depend upon ν , it is necessary that a significant fraction of the molecules evaporate from the wire before they dissociate.

Molecules incident in excited vibrational states have a kinetic advantage because the average time required to attain the dissociation energy decreases with increasing initial vibrational energy. A smaller fraction is therefore lost by evaporation before dissociation, so that I_v/N_v is expected to increase with ν . Thus the evaporation rate effectively defines a time scale with which to measure the progress of the energy-transfer processes leading to dissociation.

Model for the Reaction.—We now adopt a simple phenomenological model for the reaction process to illustrate the above considerations and to obtain a quantitative comparison with equation (2). The basic assumption is that the internal motions of adsorbed molecules are but slightly affected by interaction with the surface. The wire is regarded as an energy bath and the transfer of energy treated as in radiation theory and gas kinetics. For a weak interaction model it is readily shown that the most important energy-transfer processes involve unit changes of the vibrational quantum number and that the evaporation rate constant is sensibly independent of vibrational state.

Figure 2 is a schematic diagram of the model. The molecular-beam apparatus sends molecules in one of the four states $\nu_{\text{initial}} = i = 0, 1, 2, \text{ or } 3$ onto the wire

at a steady rate. The adsorbed molecules are distributed over vibrational states by energy exchange with the wire. Molecules in states of sufficient excitation energy dissociate and then ionize, giving a steady ion current. (For order-of-magnitude comparison, the dissociation energy of a free molecule is $41,160\text{ cm}^{-1}$, while $\nu = 715\text{ cm}^{-1}$ and the wire at $1,400^\circ\text{ K.}$ has a mean energy $kT = 970\text{ cm}^{-1}$.)

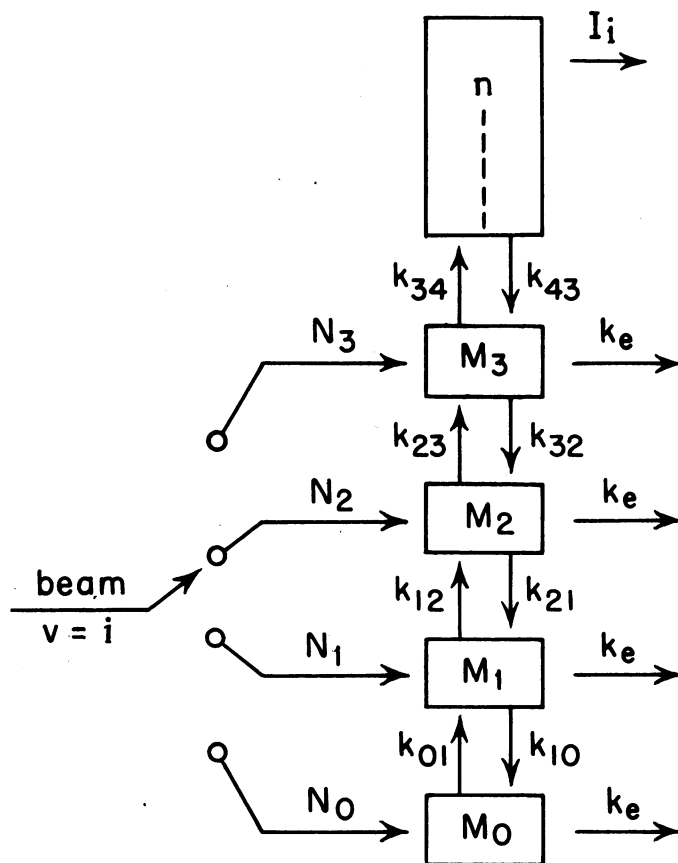


FIG. 2.—Schematic representation of the model for the reaction.

Detailed balancing of the competing processes defines the steady-state distribution of populations, $M_v(i)$. The rate of supply to the initial state is $k_s N_i$, where k_s depends upon the apparatus but not on i , since the probability of capture by the surface does not depend upon vibrational state. The rate of transitions from state v to $v + 1$ is $k_{v, v+1} M_v$, and $k_{v+1, v} M_{v+1}$ is the rate of the inverse process. The rate of evaporation is $k_e M_v$. The steady-state condition for state v is then

$$\frac{dM_v}{dt} = 0 = k_s N_i \delta_{vi} + k_{v+1, v} M_{v+1} + k_{v-1, v} M_{v-1} - (k_e + k_{v, v+1} + k_{v, v-1}) M_v, \quad (3)$$

where $\delta_{vi} = 1$ if v is the initial state i , the state being supplied by the beam, and zero otherwise.

The populations $M_v(i)$ are obtained as solutions of the array of coupled linear equations

$$\begin{array}{rcccccccl}
 v'v & 0 & 1 & 2 & 3 & 4 & \dots & \\
 0 & A_0 & k_{10} & 0 & 0 & 0 & & = C_0 \\
 1 & k_{01} & A_1 & k_{21} & 0 & 0 & & = C_1 \\
 2 & 0 & k_{12} & A_2 & k_{32} & 0 & & = C_2 \\
 3 & 0 & 0 & k_{23} & A_3 & k_{43} & & = C_3 \\
 4 & 0 & 0 & 0 & k_{34} & A_4 & & = 0 \\
 \vdots & & & & & & & \\
 \vdots & & & & & & & \\
 \vdots & & & & & & &
 \end{array} \quad (4)$$

where $-A_v = k_e + k_{v, v+1} + k_{v, v-1}$ and $C_v = -k_s N_i \delta_{vi}$; C_4 and all higher C_v are zero in the present experiment.

The populations of all states having $v > i$ are proportional to $M_i(i)$, but the population ratios are independent of i . As in Figure 2, the states above the highest state studied experimentally, $v = 3$, are considered collectively and designated "states n ." Their populations are proportional to $M_3(i)$. The states which directly dissociate are among "states n ," and therefore the ion current may be expressed as

$$I_i = K_n M_3(i), \quad (5)$$

where K_n is independent of i . The comparison with experiment is then obtained from

$$(I_i/N_i)_{\text{calculated}} = \frac{M_3(i)/N_i}{M_3(0)N_0}. \quad (6)$$

There are several relations among the rate constants which permit the evaluation of equation (6) in terms of one parameter. For excitation of molecular vibrations induced by the lattice vibrations of the surface,

$$k_{v, v+1} = (v + 1)k_{01} = (v + 1)k, \quad (7)$$

in the harmonic oscillator approximation; k is determined by properties of the molecule as well as by properties of the surface. The rate constant for the inverse process $k_{v+1, v}$ refers to both induced and spontaneous transfer of energy from the molecule to the surface and is given, as in radiation theory, by

$$\frac{k_{v, v+1}}{k_{v+1, v}} = f = \exp\left(-\frac{h\nu}{kT}\right) \quad (8)$$

For $\nu = 715 \text{ cm}^{-1}$ and $T = 1,400 \pm 200^\circ \text{ K}$, the Boltzmann factor $f = 0.48 \pm 0.05$. For the state $i = 1$, equation (6) is simply $1 + k_e/k$. We set $k_e/k = 0.4$ to fit experiment. The predictions for the two remaining states are given in Table 1. Since these are directly dependent upon the harmonic oscillator model used and also upon the value of f , the agreement with experiment is considered quite satisfactory.

In order to obtain the populations of states below $v = 3$, it is only necessary that the harmonic oscillator approximation and its consequent one quantum selection

rule extend to a few higher states. The uncoupling of equations (4) is effected by using the rapidly converging continued fraction

$$\frac{M_v}{M_{v-1}} = \frac{-k_{v-1, v}}{A_v - \frac{k_{v, v+1}k_{v+1, v}}{A_{v+1} - \frac{k_{v+1, v+2}k_{v+2, v+1}}{A_{v+2} - \dots}}}, \text{ for } v > i. \quad (9)$$

Since $k_{v, v+1}$ increases with v , evaporation becomes less important at high v ; it may be shown from equation (9) that the populations approach the equilibrium thermal distribution, $M_v/M_{v-1} \rightarrow f$, either as v increases or as $k_e \rightarrow 0$. The steady-

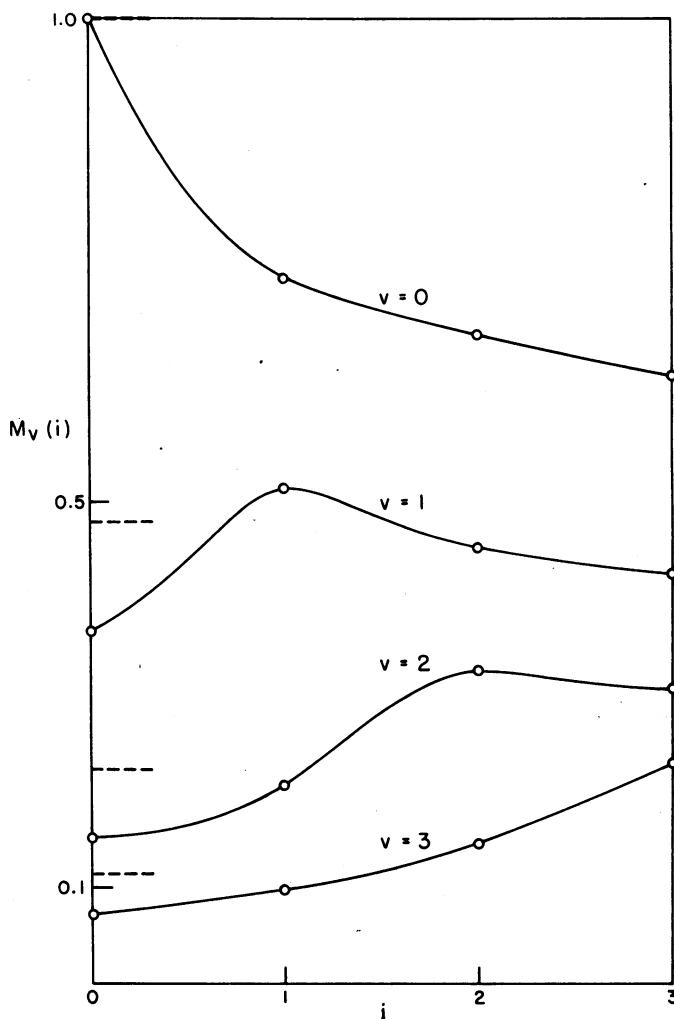


FIG. 3.—Approximate distribution of steady-state vibrational populations, $M_v(i)$, for different choices of the incident state. For $k_e/k = 0.4$, $f = 0.48$ (1,400° K.), and normalized to $N_i = 1$, $M_0(0) = 1$. The dotted lines mark the equilibrium values if there is no evaporation and no incident molecules.

state distributions as functions of the state of the incident molecules are shown in Figure 3.

We emphasize that the idealizations of the model may be relaxed as ν increases without affecting the calculations made for the lowest few vibrational levels. All states above $\nu = 3$ have been considered collectively in the calculation of the ion currents, to point out that the present experiment gives no information about processes involving these higher states and that its analysis therefore does not require detailed consideration of these states.

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INFLUENCE OF NOTOCHORD ON DIFFERENTIATION OF STRIATED MUSCLE IN AMBYSTOMA

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Much has been said in recent years regarding the influence of the notochord upon the differentiation of various other tissues in early embryos of amphibians. Following Yamada,¹⁻³ other authors⁴⁻⁷ have adopted the view that the developing notochord is in some way responsible for the establishment and maintenance of a dorsoventral gradient of "morphogenetic potential" within the embryo. This gradient is expressed in the mesodermal mantle of the trunk as the dorsal-to-ventral sequence of differentiation—myotome, pronephros, lateral plate, and blood cells. It is generally implied that the gradient results from the diffusion out from the notochord of some factor which has been termed "chorda-factor."

If some factor from the notochord is indeed necessary for the direction of differentiation of the trunk mesoderm, including the striated muscle, then, in general, the following results would be expected: (a) when the notochord is removed from early stages, muscle differentiation should be markedly inhibited; (b) when notochord is explanted with presumptive muscle tissue (viz., somite) muscle differentiation should tend to be normal; and (c) when notochord is explanted together with presumptive pronephros, induction of muscle differentiation might be expected.

It has already been shown that result *a* is not realized, for when notochord is removed from early neurulae of *Ambystoma*, differentiation of the muscle masses is little affected.⁸⁻¹¹ The notochord is obviously not necessary for muscle differentiation *in situ*.